inorganic papers

Dipotassium carbonate sesquihydrate: rerefinement against new intensity data

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Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(O–C) = 0.002 Å
R factor = 0.031
wR factor = 0.083
Data-to-parameter ratio = 21.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The redetermination of the structure of the title compound, $K_2CO_3 \cdot 1.5H_2O$, agrees with the results previously reported by Hunter & Jeffrey [*J. Chem. Phys* (1967), **47**, 3297–3302], but with improved precision. The structure is described in terms of the hydrogen-bonding network and the K–O framework, and the C—O bond lengths are compared with those found in other reported alkali carbonate hydrates.

Comment

The original synthesis and structure of the title compound was reported by Hunter & Jeffrey (1967); an aqueous solution of potassium sulfide, under a CO_2 atmosphere, produced aqueous K_2CO_3 from which crystals of $K_2CO_3 \cdot 1.5H_2O$ formed. The structure was determined using data collected on a Picker four-circle diffractometer with a 2° scan and Cu $K\alpha$ radiation.

In the present work, the compound was synthesized as a by-product in a potassium sulfoarsenate synthesis performed in air, and hence is likely to have formed by a similar route to that previously described. The large clear crystals were soluble in the normal cyanoacrylate glue used to mount crystals, so a
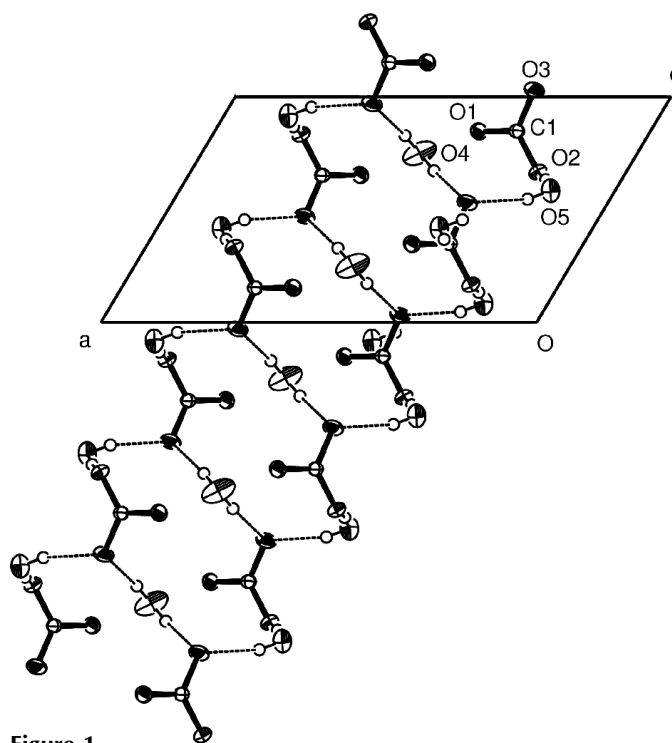

Figure 1
The hydrogen-bonded chains formed from water and carbonate groups, together with the numbering scheme. Non-H atoms are shown at the 50% probability level and H as small circles. Dashed lines represent hydrogen bonds.
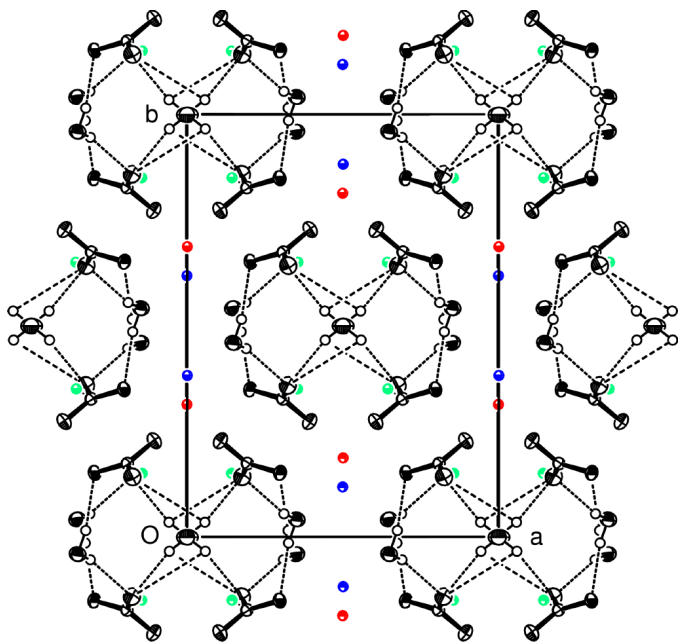
Figure 2
Location of potassium ions between and within the hydrogen-bonded chains. K1 = blue, K2 = red, K3 = green. Representation otherwise as Fig. 1.
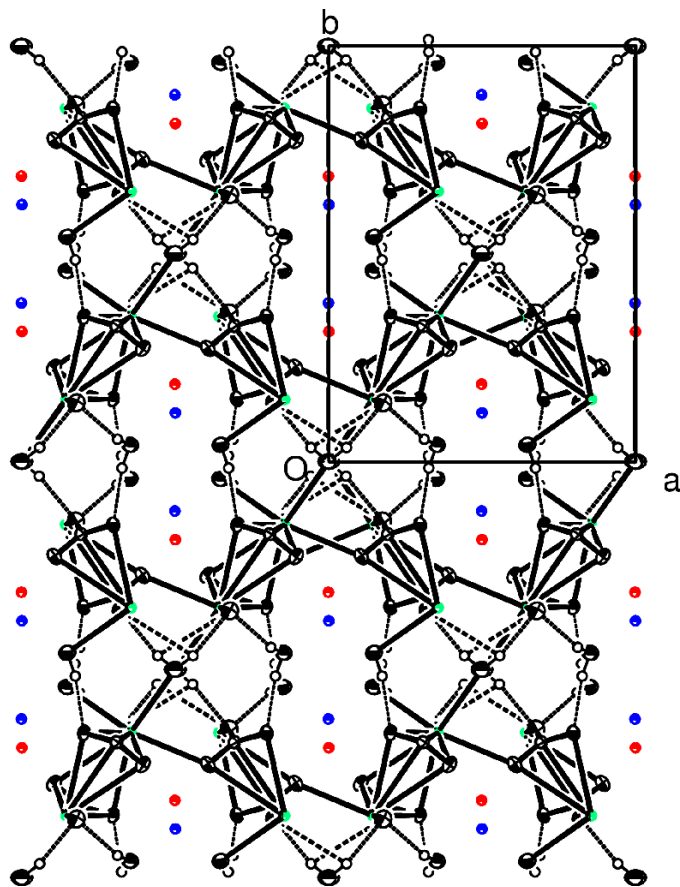

Figure 3
View of the structure as a framework in which K1 connects the hydrogen-bonded chains into a three-dimensional framework, with K2 and K3 located within the channels. Representation as in Fig. 2.

polyvinyl pyrrolidone (PVP) based glue was used instead.

The structure was solved independently to confirm the original structure determination, then atoms were numbered according to the original determination. All H atoms were located from a difference Fourier map. Bonding was analysed using both *SHELXL*97 (Sheldrick, 1997) and *PLATON* (Spek, 2000).

The structure may be described in terms of the hydrogen-bonding network. The water molecule O4 sits on a twofold axis and participates in hydrogen bonds bridging between O3 of two symmetry-related CO_3^{2-} anions, whereas the other water O5 acts as a donor to both O2 and O3. O1 is not involved in hydrogen bonding. This leads to the formation of chains along (010), as shown in Fig. 1.

The position of the potassium ions relative to the CO_3–H_2O chains is shown in Fig. 2. K3 is located within the hydrogen-bonded chains and links the chains, so it is also possible to consider the structure as a framework of K3, carbonate and water with K1 and K2 sitting on a twofold axis within the channels (Fig. 3). Equally, the structure can be described as a K–O framework with water (O4) sitting within the channels (Fig. 4). The K–O polyhedral framework is also shown in Fig. 5; in this representation O4 is involved in the coordination to potassium, and hence the channels are small.

In the original structure determination, it was noted that the C—O2 and C—O3 bond lengths were equal, but that of C—O1 was shorter by 2.7σ. It was suggested that this was due to the fact that O1 is not involved in hydrogen bonding, but the result was perceived to be at the borderline of significance. In the current determination, whilst the bond lengths are remarkably similar to those in the original determination, the improved precision means that the C—O1 bond is shorter by 16.2σ, which is clearly significant.

Comparison with other alkali carbonates was also limited in the original report since only the structures of the bicarbonates $NaHCO_3$ and $Na_2CO_3\cdot NaHCO_3$ had been determined. A search on the Inorganic Crystal Structure Database (ICSD), implemented through the UK Chemical Database Service (Fletcher *et al.*, 1996), for alkali carbonate hydrates identified six structures which have been reported since 1970: $Na_2(CO_3)(H_2O)$ (Wu & Brown, 1975), $Na_3H(CO_3)_3(H_2O)_2$ (Choi & Mighell, 1982), $Na_2(CO_3)(H_2O)_7$ (Betzel *et al.*, 1982), $Na_5(CO_3)(HCO_3)_3$ (Fernandes *et al.*, 1990), $Rb_4(HCO_3)_2$-$(CO_3)(H_2O)$ and $K_4(HCO_3)_2(CO_3)(H_2O)$ (Cirpus & Adam, 1995). Examining the carbonate bond lengths and the hydrogen-bonding network in these compounds is, again, inconclusive. In $Na_3(HCO_3)_3(H_2O)_2$ (Choi & Mighell, 1982), there are three different oxygen environments; O1 is a hydrogen-bond acceptor [C—O = 1.272 (1) Å], O2 is a bicarbonate hydroxyl oxygen [C—O = 1.309 (1) Å] and O3 is non-hydrogen-bonded [C—O = 1.262 (1) Å]. These values would tend to support the theory proposed by Hunter & Jeffrey (1967), in that the C—O bond length is proportional to the strength of the O—H interaction. However, for $Na_2(CO_3)(H_2O)$ (Wu & Brown, 1975), the C—O bond length for the non-hydrogen-bonded oxygen [1.277 (4) Å] is the same, within 1σ, as that for one of the hydrogen-bond

acceptors [1.278 (3)] Å, and only slightly shorter than the other acceptor, 1.286 (3) Å. Finally, the C—O bond lengths for C—O with hydrogen-bond acceptors O in $Rb_4(HCO_3)_2$-$(CO_3)(H_2O)$ (Cirpus & Adam, 1995) show no trend. In the carbonate group, the acceptor oxygen O2 does have a significantly longer C—O bond length than the non-hydrogen-bonded O1 [1.294 (4) and 1.263 (7) Å, respectively]. However, in the bicarbonate group, whilst the hydroxyl oxygen has a long C—O bond length [1.340 (5) Å] the hydrogen-bond acceptor O5 and the non-hydrogen-bonded O4 have very similar C—O distances, 1.248 (5) and 1.255 (5) Å respectively. Thus, whilst the influence of the bicarbonate H on the C—O bond length is evident, the influence of a donor H atom on the carbonate group C—O bond length in these structures is much less clear.

Experimental

1.10 g of KOH pellets were dissolved in 20 ml deionized water. 0.20 g of powdered realgar (later found to be a mixture of opiment, As_2S_3, and realgar, As_2S_2) was then added to the solution and heated to 1273 K for 20 min in a boiling tube on a heating mantle. The solution changed from orange to brown in colour almost immediately. After being allowed to cool, the solution was heated to 1273 K for a further 20 min then cooled again. It was then heated at 1273 K for 10 min; this was repeated three more times with cooling periods after each heating. A black–brown solution appeared during heating and during cooling a black solid settled at the bottom of the tube below a clear liquid. The solution was left unstoppered overnight. The clear liquid was poured off and the black solid was poured into a dish and left to dry. A small volume of the liquid was cooled to approximately 277 K and evaporated on a rotary evaporator. Clear colourless crystals resulted which were scraped out and allowed to dry in a desiccator. When constant mass was achieved the crystals were transferred to a sample tube and stored in the fridge.

Figure 4
The K–O framework, with O4 (water) located at the centre of the channels. Representation as in Fig. 2.

Crystal data

$K_4(CO_3)_2\cdot 3H_2O$	$D_x = 2.212$ Mg m^{-3}
$M_r = 330.47$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 3493
$a = 11.8175$ (6) Å	reflections
$b = 13.7466$ (7) Å	$\theta = 2.5$–32.4°
$c = 7.1093$ (4) Å	$\mu = 1.82$ mm^{-1}
$\beta = 120.769$ (1)°	$T = 298$ (2) K
$V = 992.34$ (9) Å^3	Block, colourless
$Z = 4$	$0.40 \times 0.20 \times 0.15$ mm

Data collection

Bruker SMART1000 CCD area-detector diffractometer	1790 independent reflections
	1618 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.045$
Absorption correction: multi-scan	$\theta_{max} = 32.5$°
(*SADABS*; Bruker, 1999)	$h = -15 \rightarrow 17$
$T_{min} = 0.576$, $T_{max} = 0.761$	$k = -14 \rightarrow 20$
4924 measured reflections	$l = -10 \rightarrow 10$

Refinement

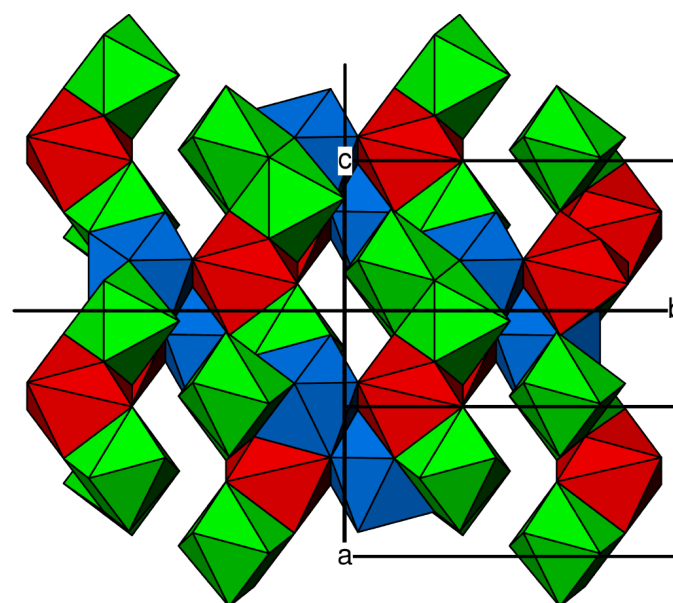|	
Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0533P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.031$	$+ 0.0526P]$
$wR(F^2) = 0.083$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} < 0.001$
1790 reflections	$\Delta\rho_{max} = 0.55$ e Å^{-3}
83 parameters	$\Delta\rho_{min} = -0.43$ e Å^{-3}
All H-atom parameters refined	Extinction correction: *SHELXL*97
	Extinction coefficient: 0.0204 (14)

Figure 5
Framework formed from K–O polyhedra. Polyhedra are coloured as for potassium in Fig. 2.

Table 1
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O4—H4$A\cdots$O3^{i}	0.77 (2)	1.93 (2)	2.6862 (17)	166 (2)
O5—H5$A\cdots$O2^{ii}	0.83 (2)	1.90 (2)	2.7135 (13)	165 (2)
O5—H5$B\cdots$O3^{iii}	0.69 (3)	2.03 (3)	2.6709 (14)	154 (3)

Symmetry codes: (i) $-x, -y, -z$; (ii) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (iii) $\frac{1}{2} - x, \frac{1}{2} - y, -z$.

All H atoms were located from a difference Fourier map and refined freely.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEX* in *OSCAIL* (McArdle, 1994, 2000), *ATOMS* (Dowty, 1999) and *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

References

Betzel, C., Saenger, W. & Loewus, D. (1982). *Acta Cryst.* B**38**, 2802–2804.

Bruker (1999). *SADABS*, *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.

Choi, C. S. & Mighell, A. D. (1982). *Acta Cryst.* B**38**, 2874–2876.

Cirpus, V. & Adam, A. (1995). *Z. Anorg. Allg. Chem.* **621**, 1197–1204.

Dowty, E. (1999). *ATOMS for Windows*. Version 5.0.7. Shape Software, 521 Hidden Valley Road, Kingsport, TN 37663, USA.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Fernandes, N. G., Tellgren, R. & Olovsson, I. (1990). *Acta Cryst.* B**46**, 466–474.

Fletcher, D. A., McMeeking, R. F. & Parkin, D. (1996). *J. Chem. Inf. Comput. Sci.* **36**, 746–749.

Hunter, F. D. & Jeffrey, G. A. (1967). *J. Chem. Phys.* **47**, 3297–3302.

McArdle, P. (1994). *J. Appl. Cryst.* **27**, 438–439.

McArdle, P. (2000). *OSCAIL for Windows*. National University of Ireland, Galway, Ireland.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.

Spek, A. L. (2000). *PLATON*. 2000 version. University of Utrecht, The Netherlands.

Wu, K. K. & Brown, I. D. (1975). *Acta Cryst.* B**31**, 890–892.